UNIVERSITY OF PENNSYLVANIA

HYDROLYSIS OF ETHYL ACETATE IN SALT SOLUTIONS OF TRICHLOROACETIC ACID

EUGENE R. MANNING

A THESIS

IN CHEMISTRY

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

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I. Introduction

During recent years the problem of the theoretical interpretation of catalyzed reactions has been given considerable attention. A number of theories have been offered; each one of them was designed to account for or summarize certain experimental results. In the course of time these theories have changed in order to reach an ever-increasing range of validity.

One of the first modern theories of catalyzed reactions in solutions of strong electrolytes was the so-called dual theory, developed by Senter and Acree. Later it was taken up by Goldschmidt, Lapworth, Taylor and others. It was partially founded on the assumed validity of the classical theory of strong electrolytes as given by Arrhenius.[1] The velocity of the reaction was said to be a function of two factors. In addition to the activity of the catalyzing ion, the undissociated molecules present had a catalytic activity of their own. At first many investigators considered this theory to have a general validity, but by others, as Bjerrum, Harned, and Åkerlöf, its value soon began to be doubted and the theory regarded as a misconception of the experimental facts. Therefore, in recent years, the reaction velocity has been considered either as a function of the thermodynamic activities of the catalyzing ions or the concentration of these ions.

When all the electrolytes present may be considered as completely dissociated, the activity rate theory as proposed by W. C. McC. Lewis, Harned and others, has been found to be applicable to the measurements for a number of reactions. Harned, Åkerlöf, and Harned and Pfanstiel showed this for the hydrolysis of ethyl acetate, Harned and Seltz for the conversion of acetyl-chloro-amino-benzene, and Åkerlöf[2] for the decomposition of diacetone alcohol.

[1] A complete list of the literature in this field is given by Brönsted, Festskrift, Köbenhavns Universitet, 1926. Here only later references will be given.

[2] Åkerlöf, *Jour. Amer. Chem. Soc.*, 48, 3046 (1926).

Harned[1] has shown that if the catalyzing ion belongs to a weak electrolyte, such as acetic or formic acid, it is most probably the concentration of the catalyzing ion and not its activity which determines the reation velocity. It must then be apparent that somewhere between the range for weak electrolytes on the one extreme and strong ones on the other, there might be either a gradual passing or a sudden change from a concentration to an activity law. Therefore, it was regarded as being of considerable interest to measure the hydrolysis of ethyl acetate in a number of acid-salt solutions, where the activity of the acids used should represent a continuous change in equilibrium constant. As a part of this program, some measurements of the hydrolysis of ethyl acetate in salt solutions of trichloroacetic acid were carried out.

II. Materials, Apparatus and Method of Measurement

All salts used were of the best grade of analyzed chemicals which could be obtained. In cases where there was no fear of decomposition upon heating, the salts were dried at a suitable temperature. Other salts were used in solution. These were analyzed gravimetrically according to standard methods. The analysis was checked by determining the specific gravity. The neutrality of the salts and the solutions was tested carefully by the usual methods. The trichloroacetic acid was tested repeatedly for the presence of chloride ion. The tests gave either clear solutions or only a very slight turbidity. Variations in the temperature of the water in the thermostat used for the measurements could hardly be detected on a Beckmann thermometer over the entire period of a complete measurement.

For the measurement, 2 cc. of ethyl acetate was added to the acid-salt solution and well mixed through vigorous shaking. Ten or fifteen minutes after the solution had been placed in the thermostat the first sample was taken. For every solution about eight samples were taken at suitable intervals of time. All samples were immediately mixed with a solution of potassium acetate. The amount of this salt introduced was approximately equivalent

[1] Harned, *Jour. Amer. Chem. Soc.*, 49, 1 (1927).

to the acid formed at complete hydrolysis of the ethyl acetate. The infinity values were measured two or three weeks after the last sample had been taken. For this purpose the solutions were replaced in the thermostat and the mean of two titrations used as a final value.

This method was followed for all solutions with small acid concentration. A few measurements were carried out, however, for solutions with acid concentrations up to two normal. Due to the large amount of acid present in these solutions the method had to be slightly modified. A sodium hydroxide solution was standardized against the acid solution in such a way that when a sample of each was used they gave a neutral or very slightly acid solution. The titration sample was mixed with the hydroxide solution immediately and the hydrolysis rate, therefore, decreased to a negligible value.

III. Experimental Results

The experimental results are given in Tables I and II. Table I gives the measurements for solutions with constant acid and

Table I

The Velocity of Hydrolysis of Ethyl Acetate in Salt Solutions of 0.1*N* Trichloroacetic Acid

Values of $K \times 10^5$

N	KBr	KCl	NaCl	$BaCl_2$	$SrCl_2$	$CaCl_2$	LiCl	$MgCl_2$
0.0	30.3	30.3	30.3	30.3	30.3	30.3	30.3	30.3
0.5	...	32.7	33.9	33.5	34.1	36.3	34.8	35.6
1.0	33.1	35.3	36.0	36.5	37.2	39.3	38.9	41.0
1.5	34.9	37.3	38.4	39.1	40.8	41.4	43.0	44.6
2.0	36.5	39.8	41.4	43.1	44.8	44.8	...	50.3
2.5	37.3	41.8	43.9	44.4	47.7	50.3	...	55.7
3.0	39.3	43.9	46.7	50.3	51.6	53.8	...	59.8
3.5	40.2	46.1	49.5	51.7	55.4	57.2	...	...
4.0	41.6	47.8	51.7	...	58.7	...	...	...

N	K_2SO_4	*N*	Na_2SO_4	Li_2SO_4	$MgSO_4$
0.00	30.3	0.0	30.3	30.3	30.3
0.05	24.7	0.5	11.5	12.0	15.6
0.10	21.7	1.0	9.7	10.9	13.5
0.20	17.3	1.5	9.1	10.3	13.1
0.40	12.5	2.0	9.0	10.4	13.5
0.60	9.8	2.5	8.9	10.7	13.7
0.80	9.5	3.0	...	10.8	14.5
1.00	8.4	3.5	...	10.9	15.0
...	...	4.0	...	11.1	16.2

varying salt concentration. Table II gives the measurements for solutions with varying acid concentration and constant total molarity. All salt concentrations are given in weight normality.

TABLE II
Hydrolysis of Ethyl Acetate

In Pure Trichloroacetic Acid Solutions		In Acid-Neutral Salt Solutions of Constant Total Molarity		
Molarity		Molarity		
Acid	$K \times 10^5$	Acid	Salt	$K \times 10^5$
0.1	30.3	0.2	1.8	74.0
0.2	56.4	0.4	1.6	121.9
0.4	89.6	0.6	1.4	163.0
0.6	128.5	0.8	1.2	181.6
0.8	149.0	1.0	1.0	195.3
1.0	177.4	1.2	0.8	209.3
1.2	191.3	1.4	0.6	216.7
1.4	198.5	1.6	0.4	217.2
1.6	202.3	1.8	0.2	217.4
1.8	210.8	..	..	....
2.0	213.2	..	..	....

The average error of the results is probably not less than 3%. In the calculations the minute was used as the unit of time. All measurements were carried out at 25°.

IV. Discussion

A graphical representation of the results is given in Figures I and II. Figure I gives the curves for the velocity of hydrolysis of ethyl acetate in salt solutions of 0.1*N* trichloroacetic acid. It appears that for all acid-salt solutions where the reaction velocity increases with increasing salt concentration, the measurements give a linear variation within the experimental error. The curves for these solutions are represented, therefore, by straight lines. Figure II gives the curves for the velocity of hydrolysis of ethyl acetate in pure trichloroacetic acid solutions of increasing concentration for acid-sodium chloride solutions with a constant total molarity of two.

Measurements of the hydrolysis of ethyl acetate have been carried out by Harned, Åkerlöf and others in other acid-salt solutions. In Figures III and IV are given the curves for the measurements of Åkerlöf with salt solutions in 0.05*N* hydrochloric and in 0.05*N* sulfuric acid. A comparison of these curves

with those in Figure I shows that the relative distribution of the corresponding curves in both cases is exactly the same. Further, the form of the curves for solutions of the same salt is nearly identical. Åkerlöf used volume instead of weight normality which may account, in part, for the slight differences in the form of the curves.

The increase in the reaction velocity with increasing concentration of the alkali and alkaline earth chlorides, for salts of the same valence type, seems in all cases to follow the thermodynamic activities of the salts added in such a way that the salt with the highest activity gives the largest increase. An exception to this rule is the behavior of potassium bromide and chloride. At corresponding concentrations the former salt undoubtedly has a higher activity than potassium chloride. It was found, however, that the velocity increase was considerably less for the bromide than for the chloride.

For the sulfate solutions the velocity first decreased very rapidly. This decrease may be due to the formation of HSO_4^- ions. At the same concentration it is greatest for the solution where the salt present has the smallest activity coefficient. This is, in a certain way, analogous to the results found for the alkali and alkaline earth chloride solutions.

The curve for the measurements with pure trichloroacetic acid solutions of varying concentration shows a distinct difference from the curve for the reaction velocity in hydrochloric acid solutions. The curve for the measurements in hydrochloric acid solutions is given in Figure V. It appears to be an almost straight line. For trichloroacetic acid solutions the slope of the curve soon begins to fall off with increasing concentration. At high concentrations the curve seems to approach a limiting value for the reaction velocity.

V. Summary

Measurements of the velocity of hydrolysis of ethyl acetate at 25° in salt solutions of 0.1*N* trichloroacetic acid, pure trichloroacetic acid, and trichloroacetic acid-sodium chloride solutions with a constant total molarity of two have been carried out. The results are of the same character, in general, as those obtained for hydrochloric acid-salt solutions.

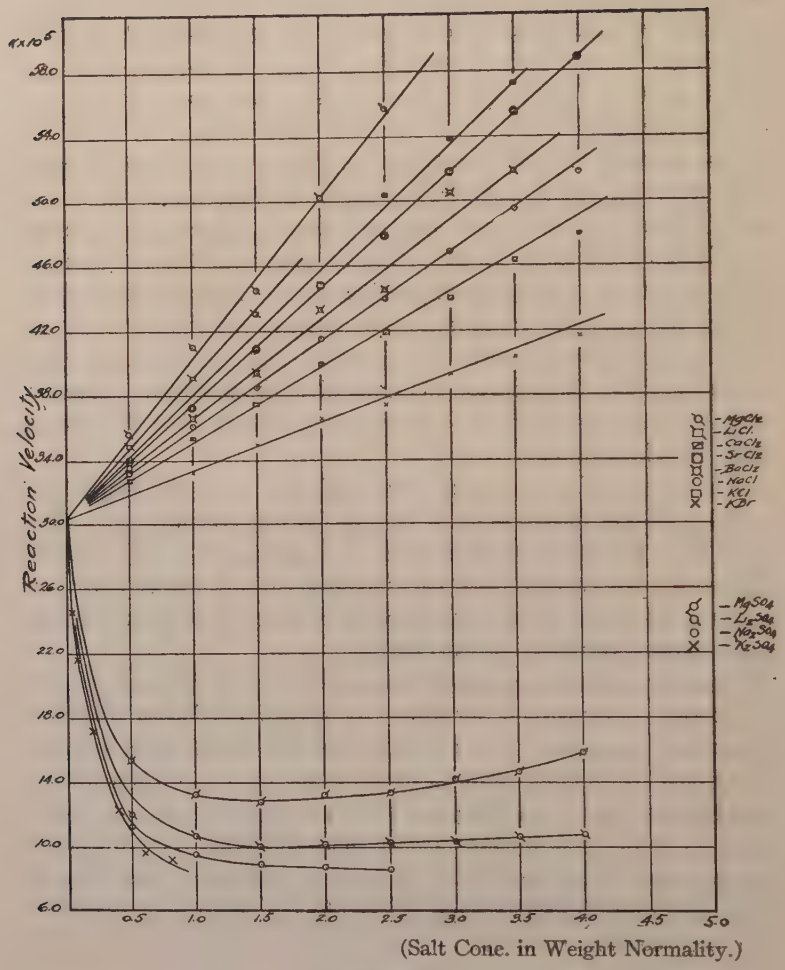

FIGURE I.

Curves for the Velocity of Hydrolysis of Ethyl Acetate in Salt Solutions of 0.1*N* Trichloroacetic Acid.

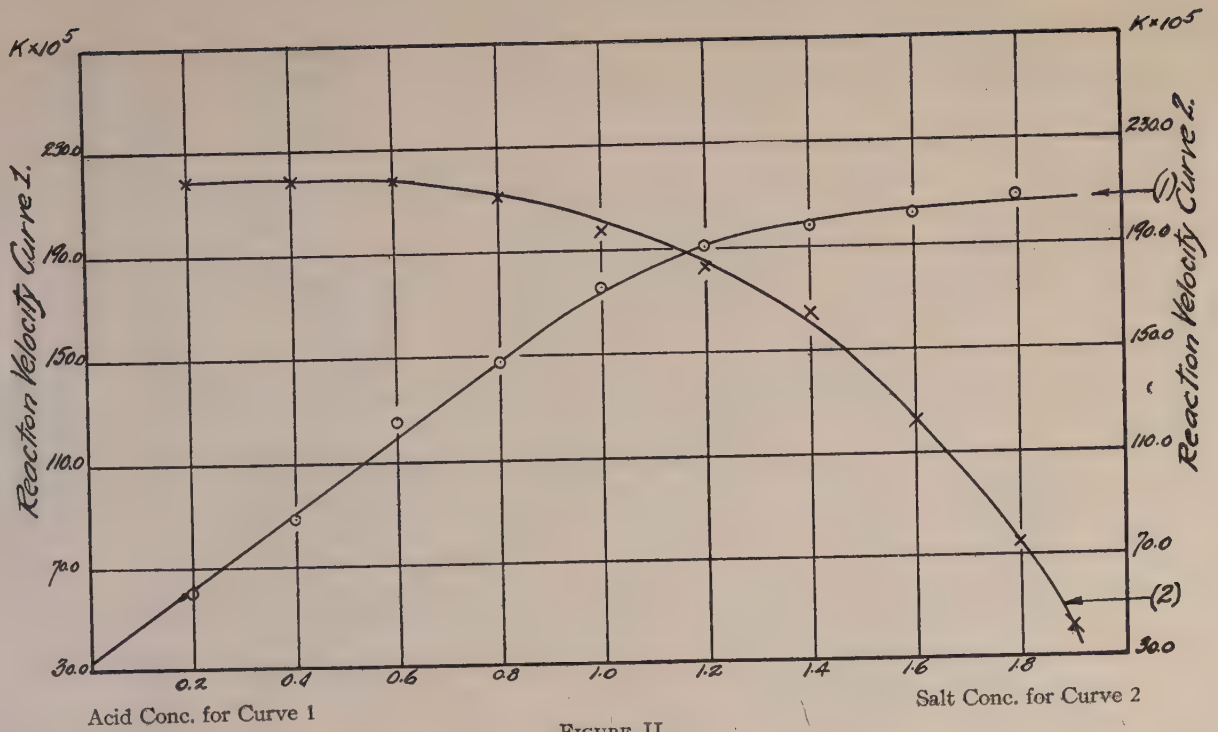

FIGURE II.

Hydrolysis of Ethyl Acetate

(1) In Pure Trichloroacetic Acid.
(2) In Acid—Sodium Chloride Solutions of Constant Total Molarity.

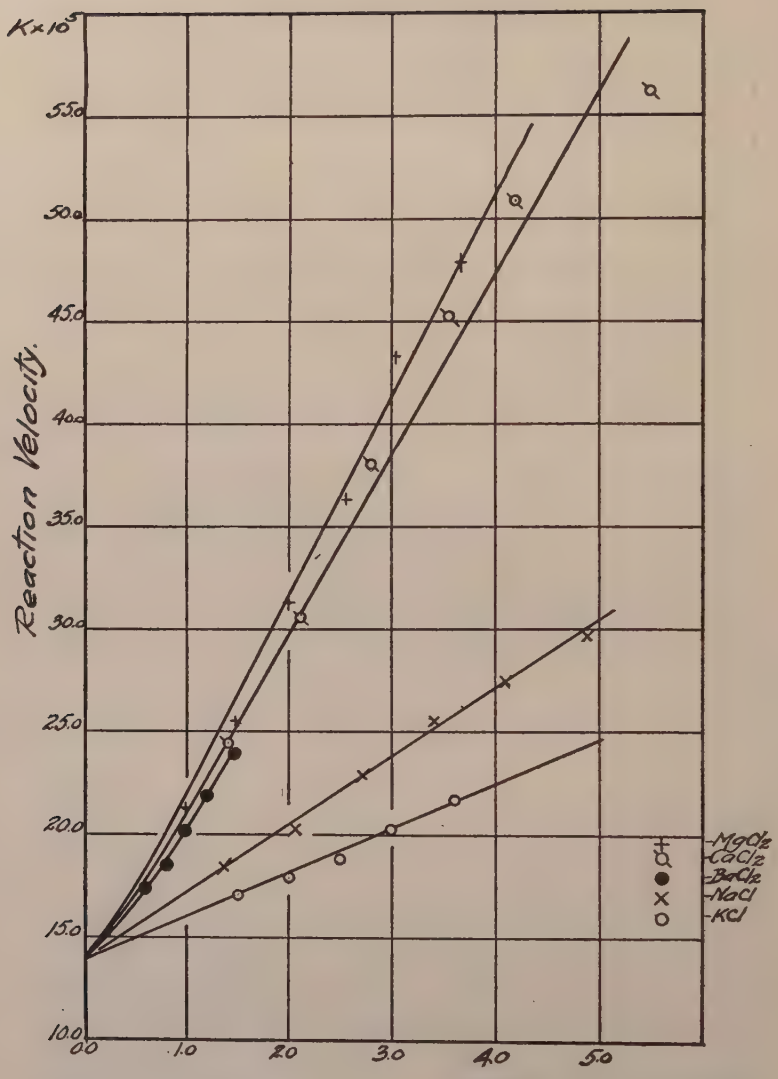

FIGURE III.

Hydrolysis of Ethyl Acetate

[Åkerlöf, *Zeit. physik. Chem.*, 98, 260 (1921).]

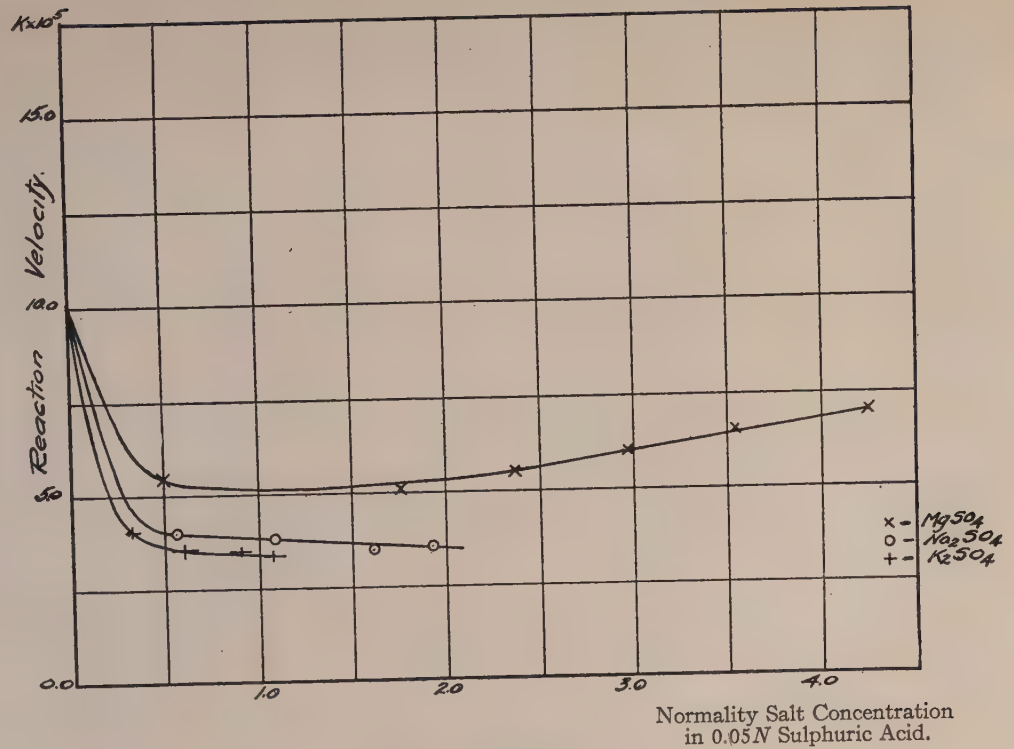

FIGURE IV.

Hydrolysis of Ethyl Acetate

[Åkerlöf, *Zeit. physik Chem.*, 98, 260 (1921).]

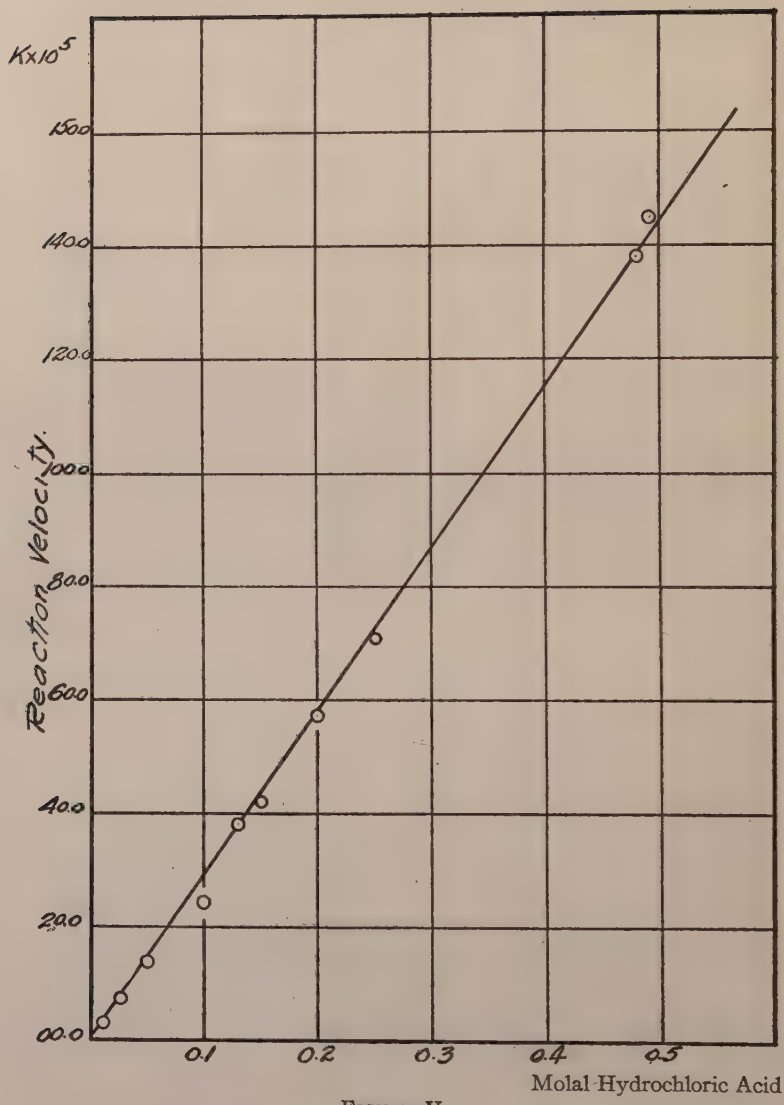

FIGURE V.

Hydrolysis of Ethyl Acetate

[From Schreiner's Compilation, *Zeit. Anorg. Chemie*, 116, 102 (1921).]